One and Two Dimensional NMR Spectroscopy for Chemists

Prof. N Suryaprakash
NMR Research Centre
Indian Institute of Science Bangalore

Lecture - 34

Analyses of ^{1}H NMR Spectra

Welcome back all of you. In the last class, we started analyzing the proton NMR spectra of some of the simple molecules which I took as representative examples. Let us now continue further and analyse few more NMR spectra, so that you get more familiarity with the analysis. Basically, this exercise is to make you people understand what is the splitting pattern? What to look at in a spectrum before you start the analysis.

Generally by when you start doing this step of analysis of couple of spectra, you will get a feel for where to see certain functional groups in the molecule and looking at the pattern you should understand what is immediate neighborhood which it is coupled, to which is giving rise to multiplicity pattern, and start and interpreting that, so that you can go ahead and generate a sort of a molecular structure in the sense, you can start assigning the peaks and get what is the molecule you are looking at.

This is basically what you can do in the analysis part. Of course if you want to get more information, you can even analyze the multiplicity pattern very carefully, so that you can get the J coupling information also. That is also possible, but again, we will continue like this, with the analysis part

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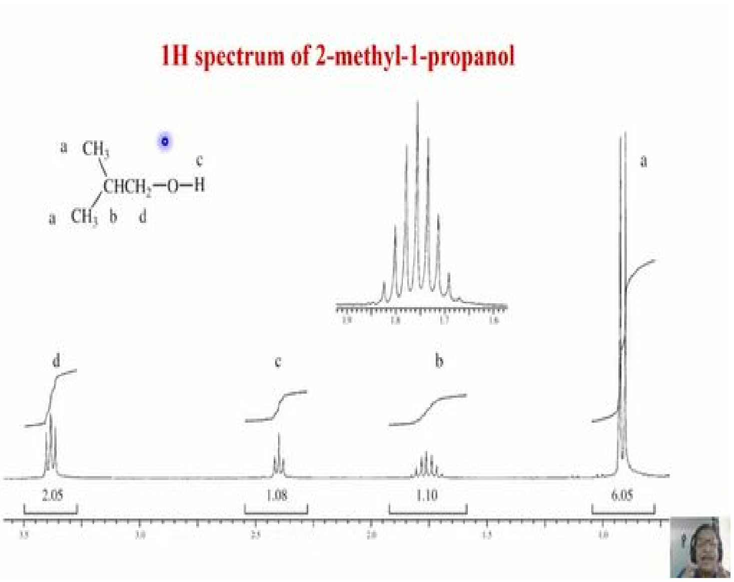

This is a simple molecule. It is the 1H spectrum of 2-methyl-1- propanol spectrum taken from Pavia book, edition 4. Look at this one, this is structure of the molecule. Of course look at the molecule, how many types of different protons are there, chemically in-equivalent protons, that is the first thing you have to count before you start the analysis.

First here is OH proton, that is one; we have one CH2 group, which is different because they attached to OH and another CH here, you have another CH group, which is different from CH2. We also have two CH3, possibly they are equal. Now, we have to start looking at where these protons peaks do appear in the proton NMR spectrum. Let us start from the right side of this molecule OH proton. Normally OH protons and NH protons are labile protons. They will generally do not experience couplings so easily, it gives rise to broad hump, especially OH proton gives rise to broad hump even though it is attached to the neighboring other group of spins like CH, CH2. Couplings are, very rarely seen. Not that it is not there, it is there, but you have to take special precautions while doing the experiment, so that you can see this splitting pattern. So does not matter, but if you look at this spectrum, there is no broad peak, you can see here.

So, OH if it was there you would have seen as a broad peak. Generally, in all the proton spectrum of several molecules you see in various books and literature, when there is a OH proton, you will be seeing a broad peak. But I don't see any peak broad peak here. We have 4 different types of protons, we have 4 groups of peaks. That means one of them must be OH.

Now what is this OH could be? If you look at it carefully, since it is not a broad peak it might experience coupling with this CH2 protons. Quite likely, if it experience coupling with this CH2 proton, apply 2NI+4 rule; OH has to be a triplet, sure. Let us look at this spectrum, whether there is a CH3 group, I am sorry, whether there is a triplet, not CH3 sorry, whether there is a triplet. Of course, there is one triplet here.

There is also another triplet here, triplet like not exactly triplet. You please remember, the triplet intensity pattern is 1:2:1, but do they look like that. If you carefully see it is not a triplet, it looks a doublet of doublet with some extra splitting in the central peak. It appears that central peak is also split, it is not clearly visible here. The only very clear triplet pattern is seen here.

So let us assume this must be the OH proton and analyze this and start assigning this one for OH proton, so OH proton is marked c, so this is c, fine. Next is what? In the same order we will come, you will see CH2 here, Now the CH2 here is coupled to CH and also it is coupled to OH, it has to couple to OH because we have seen OH as a triplet, that means the CH2 is coupled to OH, and also the CH, two individual protons; When it is coupled to single protons, what is the pattern we expect? This one is 3 bonds away this is just 1, 2 bonds away, again we saw so 3 bonds away. So this coupling could be larger than this, if that is the case this proton splits this CH2 proton into a doublet, this proton splits the CH2 into a doublet further; because of this OH proton this will become another doublet. So doublet of doublet, where is doublet of doublet here? I do not see that is why I said, this is a triplet, if you carefully see here this, group appears as if, it is doublet of doublet this central peak is partially resolved, not fully resolved but it is not a triplet. So safely we can assume this must be the CH2, fantastic. What about CH proton? This is a very complex spectrum, it will give, this group especially.

Reason is, it is coupled to 2CH3 and also CH2. Remember the multiplicity pattern I explained to you, when one of the protons is coupled to two other many chemically equivalent spins, you worked out the multiplicity pattern. First is it is going to split because of this into a quartet and then again into a triplet, so complex multiplicity pattern we are going to see. Look at this one and that complex multiplicity pattern is somewhere here.

So this must be CH proton, very good. We can analyze that easily now. Then what is left over? So this you assigned for OH; this you are assigned for CH2; and this you assigned for CH, then what is left over? The left over is only CH3's; and look at this peak, it is a doublet, why is this a doublet? This CH3's may be equivalent chemically, but it is split into a doublet because of CH. This CH splits this into doublet. So it appears as doublet, it has to couple that is what is happening.

You can see this CH is coupled to this and also this, otherwise it could have been simply a triplet and very fact it is a complex pattern here, you must assume it is coupled to this and when you verify there are only two peaks present here; only doublet of equal intensity, these two are equivalent chemically, and it should give a single peak, but because of coupling with CH here, it is a doublet. This analysis becomes simple, very clear now.

We have assigned all the peaks, we have looked at the multiplicity pattern, and it matches with our molecular formula or the structure given.

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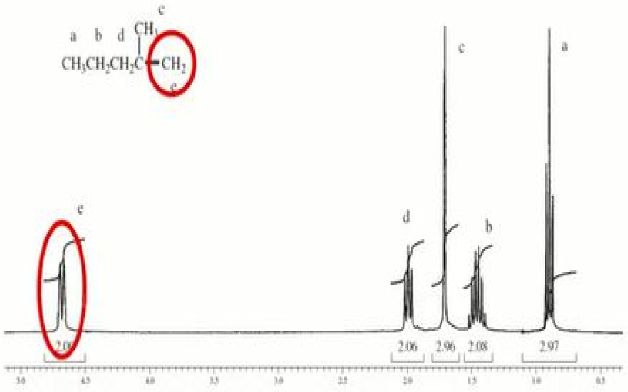
^{1}H spectrum of 2-methyl-1-pentene.



Let us go further, this is another molecule 2-methyl-1-pentene, something, it is a linear molecule look at this molecule. We will start with this, one because it is very simple to analyse. This CH3 it is coupled to CH2, as a simple reason you must get to triplet, that is analyzable, very fine, you can assign. Now, what about this CH2? It is coupled to CH3 and also CH2. This CH2, so what will happen now? As consequences this CH2 will be split into a quartet because of this CH3. Remember it is going to be it will split to a quartet because of the CH3 and further, it is going to be further split into triplet because of this CH2. So this CH2 will be the triplet of quartets or quartet of tripletsm depending upon which coupling is larger, that we already analyzed, multiplicity pattern how it comes we have discussed it long back.

So, what is that complex multiplicity pattern? See here, this has to be proton b, for a is assigned, b is assigned. Now d, what is d? d is simply a triplet because it is coupled to CH2 and there is no long range coupling it is the way triplet, and there is no long range coupling, that is assigned now; very clearly you could assign. Now, if you look at that one there is one group, one peak is there with intensity 3, look at this one intensity is nearly 3.

What is it? I already told you long back if you have a single peak of relative intensity 3, with respect to other groups it must be CH3 group which is uncoupled, what is that possibility? This is the only CH3 group which is uncoupled; as a consequence you can assign this for this CH3, That is also done now, what is left over? Left over is CH2, so this is not coupled to this, this is not coupled this, all these things are not coupled.

Then, what is the pattern we expect? When none of them are coupled, this CH2 has to be a singlet. But it is not a singlet here, what is this pattern? Why? What is this which is making this into a multiple? Something really difficult to understand. It is definitely not completely coupled to CH2, otherwise this would have become a multiplet; and definitely it is not coupled to CH2 because if you go by that, this would have been very complex. And, what is the problem? Remember, these two protons are not equivalent as a consequence it behaves AB spin system, See that is what is happening; as a consequence of that; these two protons appears as like AB protons coupled with in itself, strongly coupled.

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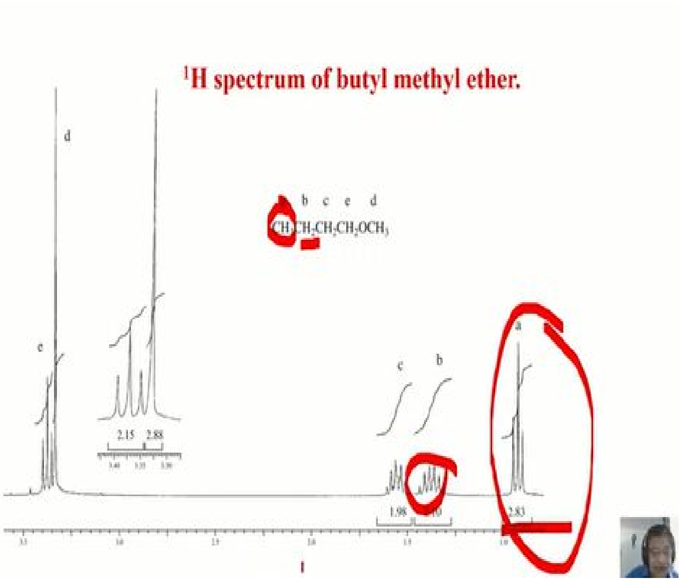

^1H spectrum of butyl methyl ether.

When we can go on interpreting like this. This is the 1H NMR spectrum of butyl methyl ether, Here nothing much to think. Very clearly we can start assigning. It is a OCH3 group not coupled to any of the protons, it must be a singlet. We can see there is only one singlet here, this is proton d; then it is not coupled anything. This CH2 is coupled to this, it has to be a triplet, see this has to be a triplet here.

This is proton e. Then this is c, this CH2 protons are coupled to CH2 here, and CH2 here is triplet of triplet, one CH2 splits this CH2 into a triplet, other CH2 will split each line of the triplet into to triplets, so it is triplet of a triplet. What is that possibility? you can see,It is only this, why not this one? See this you have to carefully observe the complexity, the complexity is much more here, it cannot be simple triplet of triplets.

That can safely be assigned to this group, because this is split in to quartet by because of CH3 and each line of quartet is split into a triplet because of CH2. it is more complex than this one that is why this is assigned to be proton b, when you understood the point, this is proton b. Now, what is left over? Only this, this has to be coupled to only a CH2 proton and is a triplet, this is methyl proton, that is CH3. very easily you can make the assignment.

Now, I am sure you would have got a hang of what to do; how to go ahead and in analysing of the spectrum, when the molecule formula is given, or when the structure is given, you can think of both; you may be given molecular formula without knowing the structure, but you have to get the structure. It is possible because when you synthesize the molecule you do not know what it is; or you may know the molecule but you do not know the structure, either way you can get ether information by the analysis of this spectrum.

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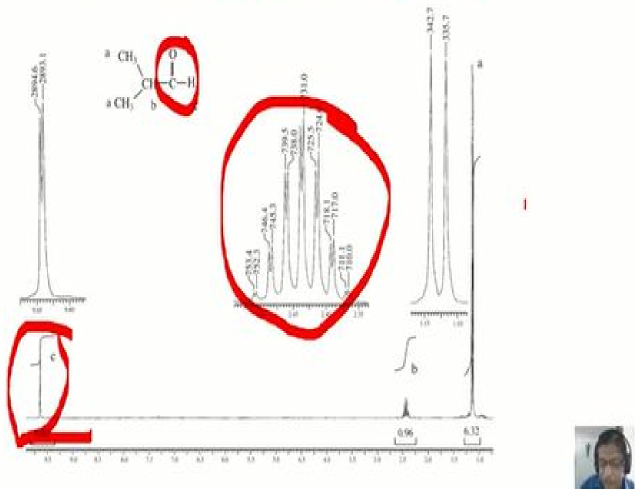

^{1}H spectrum of 2-methylpropanal (isobutyraldehyde).

So we can continue like this further, See this spectrum, it is a very simple spectrum, it is spectrum of 2-methylpropanal, very simple molecule look at the structure of this molecule; there is a CH3 group, CH group and other CH. Only 3 types of protons are there here, so you get one type spectrum, we have one group, other group, another group; very well, very clear, right? So how do you interpret this one now?

Very easy, simply look at the spectrum this CHO, where does the CHO will come? start looking at this spectrum, where do you start with? look at the intensity here, the intensity is 6.32, this must be two CH3 which is coupled to this CH proton. Which is coupled by this CH proton and maybe they are very close by chemical shift which are not resolved or equivalent.

So one big peak split to a triplet because of this, if this may not be chemically equivalent because of the structure, then they are not resolved here. If they are chemically in-equivalent we should have seen the doublet of doublet, there are 2CH3's which are well separated and each line of this will be doublet because of coupling to CH. This is a low resolution spectrum; we are not seeing, that but does not matter.

We will say there are two CH3 peaks whether equivalent or not coming at a single peak, they are split into doublet because of CH proton. Now what happened to this CH proton? very interestingly this CH proton is a very complex pattern, what is this complex pattern coming from? This CH proton remember is split by two CH3s, one CH3 splits this into a quartet and each line of this quartet is split into another quartet by this CH3. At the same time; so 4 quartet is 4 lines; 1331 intensity, again split into another quartets; each line of this quartet split two another quartet, so 16 lines you got, plus this CH proton is also coupled to this CH proton; there is a coupling between them because I can see this one, if I look at this one, the expanded region of this one, somewhere I do not know, where is it, what is this one? I am not seeing something here, I do not know what is this is written here, I will come to that to the spectrum of that later, I do not know.

Now we will look at this one, this has to coupled to this and as a consequence each line of this quartet will be a doublet, you understand this? Now we can understand how this spectrum of 2-methylpropanol can be assigned. There is some peak which is coming around 9.6 this one, this is this proton, it is 9.6 peak, correct? Now I know this CH proton. This CH proton, if you carefully see is a doublet, why this is a doublet? Because it is coupled to this.

So it is not a mistake in spectrum, it is a right spectrum only thing is I was not seeing seeing carefully. It is this proton which is split to the doublet because of this, so this proton, interestingly experiences coupling with 2 CH3's and this CH proton; and interestingly all the couplings are different. As a consequence you get 4 into 4 quartet, each line these quartet is a quartet and each of them is further split into doublet like this, you can see.

So you should get 32 peaks here; that is the reason why it is so complex, you understood the point now, what is happening here? So this is the CH proton. Now the question is why this CH proton or CHO group, why it is coming down field? Because it will attach the C double bond O, that is what you should look at in the spectrum, this is CHO group; this proton is coming down field and then CH and 2CH3. So there are three different groups you can interpret this by slitting pattern very easily.

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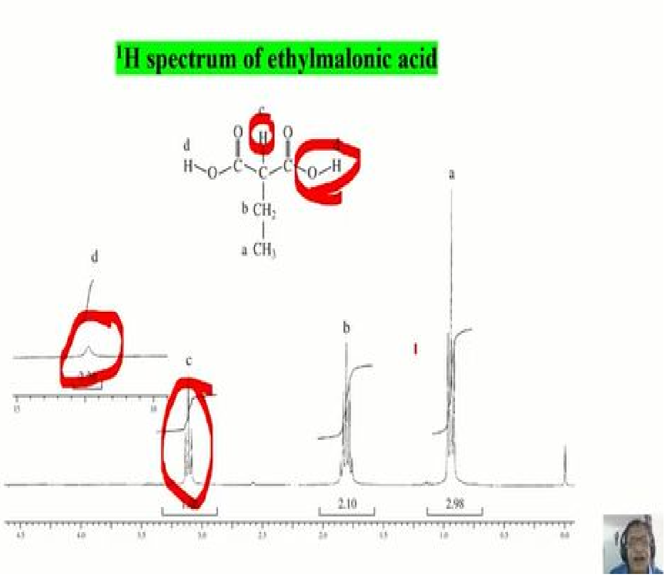

^{1}H spectrum of ethylmalonic acid

Now, this is the next example; we will take few more examples to make you highly comfortable, This is 1H spectrum of ethylmalonic acid, correct look at this structure, very beautiful structure perfect symmetry is there along this axis. Now let us start interpreting the spectrum, how many different chemically in-equivalent protons are there, this is equal to this, there is one type, and this is one, this is one, 3, and this is one, and there there are only 4 types of protons available in this molecule, which are chemically in-equivalent.

How to analyze that? Very simple, please look at this one, how do you analyze this one? this CH3 group and CH2 group very common we have been to analyzing this for quite some time. What is happening in this case and CH3 and CH2 are present, this is a CH3 group which is split into a triplet because of this CH2; but what is happening to this CH2? This is split into quartet because of this CH3; but it is not just a quartet. What is happening? It is a pentet; you see; how did this pentet come? Because each line is quartet is further split by this proton; as a consequence due to spectral overlap. We have generated pentane pattern earlier, this looks like a pentet. So this has to be proton b, this one, understand, now this is assigned, this is the assigned, what is left? This one, what is this? This is coupled to this, it has to be a triplet, see; only thing which is left over is OH.

Remember, I told you in the previous spectrum while analyzing; normally OH protons are broad, why it is broad? Will explain later when you come to relaxation etc, it is a broad spectrum you are going to get, so broad and if there is any other splitting,it is generally not seen; of course here in this case the splitting possibilities are also low, no problem, but is there something attached to that, generally it is very difficult to see this splitting, unless I said special precautions are taken in the preparation of sample, where you are going to see this also, but this is safely assigned now, so all the 4 groups of protons are assigned. I hope you are getting the feel for how to analyse the spectrum, looking at the structure, looking in the multiplicity pattern, looking at where do they come in chemical shifts, etc?

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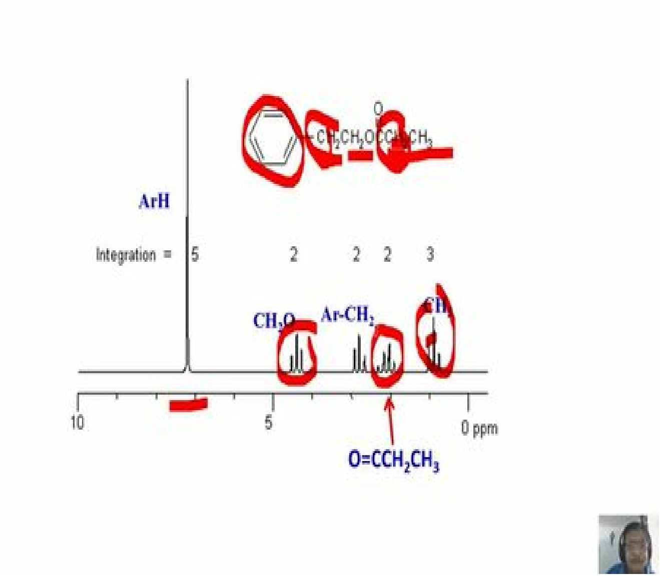

This is fairly a complex spectrum compare to previous one. Now let us analyze this together, what is the possibility here? How many groups of protons are there? Look at it very carefully this is CH3, one proton, this is one, and they are chemically in-equivalent and in between CC double bond OCH, so there is a break and this will not couple to this, there is another proton here, another proton here and we have a phenyl group.

So 1, 2, 3, 4, 5 groups of peaks are there, count the 1, 2, 3, 4, 5 groups of peaks are there. What are the intensities? Here there are 3 protons, that is 3 here, and then 2 protons here, you have 2, another 2, another 2, and this is phenyl ring 5 protons intensity, it is fine. So the relative intensities are matching, agreeing with that, there is no problem at all. You are interpretation comes now; to interpret which is which, especially the CH2 proton.

This CH2 is also attached to O, this CH2 is attached to C double bond O. Your assignment of this CH2 and CH3 is something which you have to do correctly. Apart from that, it is pretty simple, especially look at these aromatic protons I did explain to you in the case of aromatic ring kind of thing when I explained, all those protons which are in the plane of the ring generally here come here deshielded and come but low field that is what I said, that is what is happening?

So peak which is coming around this, are generally aromatic protons, they come at 7 ppm around 7 for this is this ring, clear? There now of course this portion is also clear. This is CH2, this is CH3 split into a triplet because of this and there is a quartet, this CH2 splits into quartet because of this, analyzable. Now, this is attached to this; and I said this is this CH2 and next is, this is CH2 attached to O, comes down field and it is a triplet because it is coupled to this.

Then, this CH2 is coupled with this, that has to be this, aromatic CH2. This is very important thing, you have to see, it comes because it is attached C double bond O. And in case of confusion, let us say between this CH2 and this CH2, which is coming down field? Whether this is CH2) or this one, how do you assign? Remember, this is coupled to CH3 this splitting pattern gives you J coupling measure the J coupling. This J coupling should exactly match with this or this; the one which matches with this J coupling, that is the one which is coupled to CH3, then you can identify whether that CH2 is this or this. That is another way, you understand, when you have confusion in the assignment of peak, an example like this both of CH2's, how do you know which is coming to down field; which is coming to high field, look at the coupling pattern and see which splitting pattern separation matches with this one, and that is CH2, this is a way you can start the analysis.

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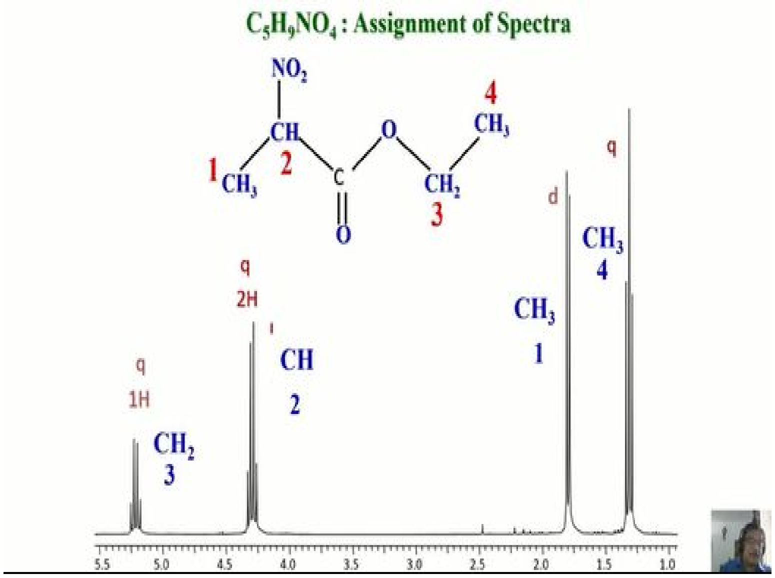
$C_5H_9NO_4$: Assignment of Spectra

Let us continue, we are slowly increasing the complexity, we are looking at the next spectrum of the molecule, which like this. This formula is known and the structure is also given, chemical structure, this is the NMR spectrum. Your life has become very simple, because everything is marked, in this case absolutely no need to spend more than 1 minute to analyze the spectrum; maximum 2 minutes, you will get this spectrum and the analysis is simple.

You know, how look at it; this CH2 and CH3 are coupled, and there is a breakage here, and the long-range coupling is not seen, they are only CH, CO, bond like this. If you see 1, 2, 3, 4, 5 bonds away, these couplings are not generally scene. So this forms one coupled system; and this form another coupled system, so you have to analyse only two coupled spin system that is all, no coupling between them, as a consequence it is very simple.

So, what you have to do? This CH3 will be a quartet, I am sorry will be a triplet, because of this and this CH2 has to be quartet because of this, where is the quartet here? There is one quartet here and there is another quartet here. Now, the question is which quartet belongs to this? You have to understand. which quartet? you have to know understand, go by the intensity. This is also quartet this also quartet, but which is more intense?

Which has more intensity, This is two times the intensity, compared to this, remember this. So this must be a quartet where this group attached to 2 protons. Then what it is? It has to be this quartet, which has to be this, which is coupled to CH3. So, this is a CH2, the CH2 correspond to this, this CH3 correspond to this, fine ; done. What is left over? Only this and this, then this CH3 has to be a doublet, because it is coupled to CH, so this is doublet. So this is CH3 then what about this CH? Is a quartet, see this is a quartet. So only thing in this case it distinguishes the two quartets which belong to which, you looked at the intensity. There is 1 intensity, there is 2 intensity; that is another way of identifying the coupled patterns. If you have a difficulty again, you can measure the J coupling that is also possible. So these are the ways you can start analyzing these things.

Now, more or less we have assigned all the peaks in this molecule, this is CH3 one, this is CH two, this is CH2 three, this is CH3 four, this a very fairly simple molecule; in this case I gave an example because both are quartets, you have to take into account the intensity pattern to identify whether this quartet is belonging to this or this, that is all. That is the only difference here, next analysis is very simple we get the coupling pattern, we can do that.

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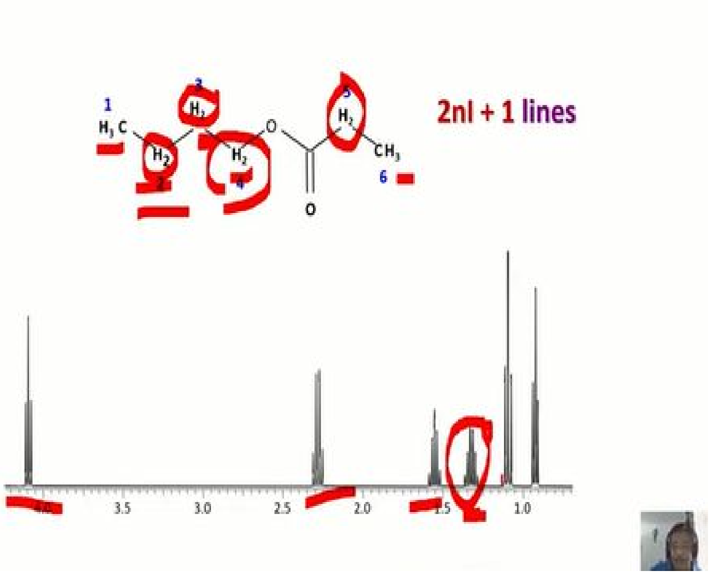
2nI + 1 lines

This is the next complex molecule, now I am increasing in the complexity slowly, one by one. Look at this one now, how many groups of protons are there? 6, this is 1, 2, 3, 4, 5 and 6, this is the spectrum, now start interpreting; very easily you can interpret, if you look at the spectrum there are well discriminated peaks are there, you know discriminated peaks are there, very, very well dispersed 1, 2, 3, 4, 5 groups of 6 groups of protons are there.

But remember there is a CO here. If I take this proton H2, there is one bond, two bond, three bond, four bond, five bonds away, this proton coupling to this proton probability is very, very low. I do not say this proton can couple to this because they bare several bonds away. So, that means you can distinguish this is one coupled partner; this is particular coupled spin system, you can identify this one spin system; and remaining four are another spin systems, very easy.

Now you are distinguished two spin systems here, this is easy to analyse of course CH2, CH3 right from yesterday we have been getting triplet or quartet. Now this has to be a triplet, this has to be a quartet; which is which? There is one triplet here and one quartet here, this quartet is easily assigned, this has to be this CH2. Now this CH3; there are two triplets for unfortunatel;y the reason it could be this CH3 or this CH3. You do not know how to assign this.

So, we will wait for some time; first you assign this one that is correct, that is for this CH. Now will go further, now we will come to this CH3, really this way this CH3 has to be a triplet because of this; correct? So, now we identified two triplets; allright; but one interesting thing happens; if you carefully see the triplet separations, see this triplet separation; for this when it is coupled to this quartet measure this J coupling, measure which one has a J coupling here. This separation and this separation has to match; whether it is matching for this and this that will identify which is this CH3. Alternately look at this CH3; this is coupled to CH2 it is a triplet, one of them will see later. Come to this proton, this proton is coupled to CH3 and it is a quartet, it is also coupled to CH2, what does it mean? Each line of the quartet will become a triplet and is a very complex pattern. Where do you see that complex pattern, it is here.

Now the question is, why not this? Why I am telling it is this one; you will see later. If you look at this proton this is coupled to this and this; CH3 and this CH2; It gives the quartet of a triplet or triplet of quartets depending upon the coupling strength; and whereas look at this one it is coupled to only two CH2's is in it? It is triplet of triplet, triplet of the triplet gives maximum get 9 lines; quartets of triplets, you get 12 lines, so complexity is more here.

So, I would safely say this is the CH2. And I would say this CH2 is this one. Now, what is the leftover, this CH2, it is this one; this is coupled to this, it has to be triplet. So, we assigned this quartet because of this. Now only thing left over is these two CH3, which is 1? Which is 6? That you can assign by making the J coupling measurement. Very easy, you can do that, okay? Either here or there in the multiplicity, this multiplet or this multiplet, measure the couplings you will know which CH3 is which. That way you can easily assign.

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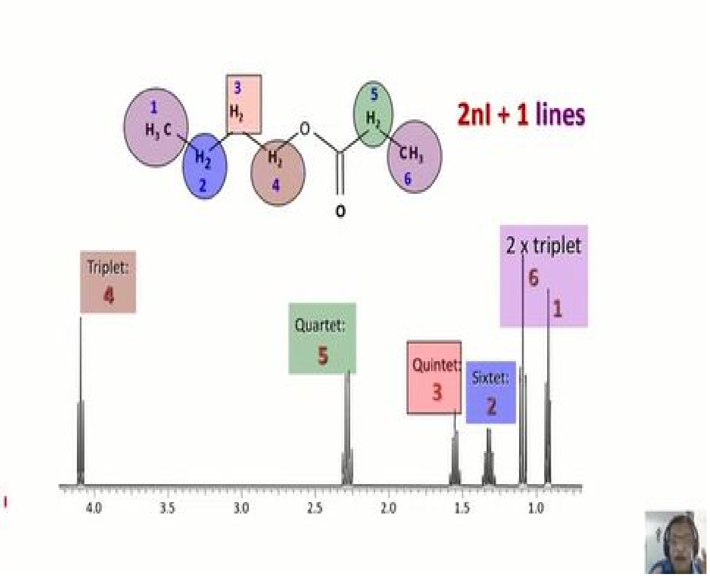

2nI + 1 lines

So, now assignment has been made and I said this is 6, and this is 1; and this is 6 it will be a sixtet and this is a quintet and it is a triplet and this is a quartet, so in this molecule you get triplet, quartet, quintet, sixtet everything you have observed here. Now, if you look at this 5 and if you look at this 6, 5 is this, this separation matches with this separation, that is why it was assigned as 6 by J coupling.

Now you got to point, how to make the assignment; this very simple molecule it is deliberately chosen because you have all possible multiplicity patterns, you can see, except doublet. Triplets quartet, quintet, sixtet everything was observed and looking at the multiplicity pattern and the complexity and the chemical shifts where it is coming you can easily assign. Of course you can use chemical shift information when this CH2 is attached to this O it has to be down field. That also you can utilize, and this CH2 is standing alone coupled to this, no other coupling. So, it has to be CH2 and further it is attached to oxygen, so it has to come down field; that way we can start making assignments of this spectrum.

I hope you all have understood how to make assignment. So, I am going to stop with this analysis. We will come back in the next class, let us see how to proceed further and if I find one or two complex spectrum I will show you, so that you can get more familiar and after that I will start going to the heteronuclear spectral analysis, first I will start with the carbon 13 spectrum. We should know how to analyse the carbon 13 spectrum and how to get a good carbon 13 spectrum everything; and afterwards we will go to other topics.